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CITATION:

Suito, Eiji ...[et al]. The Measurement of the Size of the Colloidal Particle by the Ultracentrifugal Method and the Electron Microscopy. Bulletin of the Institute for Chemical Research, Kyoto University 1958, 36(6): 197-205

ISSUE DATE:

1958-11-30

URL:

http://hdl.handle.net/2433/75671

The Measurement of the Size of the Colloidal Particle by the Ultracentrifugal Method and the Electron Microscopy

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Received October 30, 1958

The particle size of the lyophobic colloid was measured by the ultracentrifugal method and compared with that obtained by the electron microscopic method. The specimens used here are five kinds of gold sols and iron hydroxide sol.

The sedimentation photograph was taken to calculate the particle size in the ultracentrifugal method. The electron micrograph was also taken and various kinds of mean diameters were calculated from the distribution curve.

The particle size obtained by the ultracentrifugal method was always smaller than that obtained by the electronmicroscopy, and the actual value is considered to exist between these two values. Because of the small deviation of these two values, the particles are considered to be well dispersed in the sol and not to take the state of cluster.

I. INTRODUCTION

Various methods have been developed for measuring the size of the finely dispersed particle ; the method using the ultracentrifuge or the electron microscope, or utilizing the B.E.T. adsorption, the small angle X-ray scattering, or the light scattering. Each method, however, seems to have been independently investigated so far. The comparison of the results obtained by different methods has not yet been carried out deeply in spite of its great importance.

It is the aim of the present work to compare the two results of measurement of the particle size of lyophobic colloid by two different methods, the ultracentrifugal method and the electron microscopy, and to clarify the limitation for the application of these two methods to the measurement of the particle size of the lyophobic colloid.

II. THE APPARATUS AND SPECIMENS

The ultracentrifuge used in the present work is the unit of PHYWE & Co., Ltd., "PHYWE-Ultrazentrifuge", having a rotor driven indirectly by the air turbin.[1] The centrifugal force is variable in a range from 100,000 G up to 260,000 G at the maximum speed of 60,000 r.p.m.

The specimen used were gold sols and iron hydroxide sol, respectively, as shown in Table 1.

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Gold sols are five kinds of Faraday's sols, which were prepared by the reduction of chlorauric acid with a small amount of pure ether and carbon disulfide solutions of phosphorus at various temperature. The particles of the Faraday's gold sols are very fine as usually known.

Iron hydroxide sol was obtained by the hydrolysis of ferric chloride solution at 100°C.

Table 1.

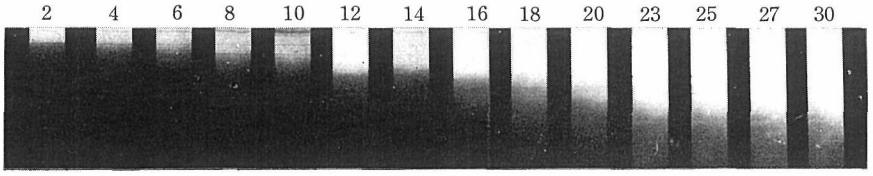
No.	Sol	Concentration (mg/l)	Temperature °C	Reagent	Maximum absorption (Å)	Measurement temperature (°C)	Rotation speed (r.p.m.)	S ($\times 10^{13}$)	D_s (Å)	D_m (Å)	D_3 (Å)
1	Au*	50	25	P-ether	5150	26	13,424	4.0	59	90	115
2	〃	〃	〃	〃	5100	24	12,956	4.8	66	110	121
3	〃	80	80	〃	5100	18.7	20,747	1.7	41	120	153
4	〃	〃	90	〃	5200	18	17,257	3.3	59	100	177 130
5	〃	〃	80	P-CS_2	5150	18.8	25,859	1.2	35	60	94
6	$Fe(OH_3)$**	86	100			20	38,299	4.2	55	120	130

* Faraday sol.
** Hydrolysis.

The concentration and the temperature of preparation of these sols are shown in Table 1. The color of these sols are bright red, dark red, and purple. The absorption spectrum curve of each sol was taken with the Beckman-spectrometer and the wave-length of the maximum absorption is also shown in Table 1.

III. EXPERIMENTAL RESULTS

Sedimentation photographs were taken with an equal exposure on slightly seperated parts of the same photographic plate at a definite interval as shown in Fig. 1. The conditions of the rotation speed of the rotor and the temperature in ultracentrifuge are shown in Table 1. The procedure for the calculation of the particle size using these sedimentation photographs mainly depended



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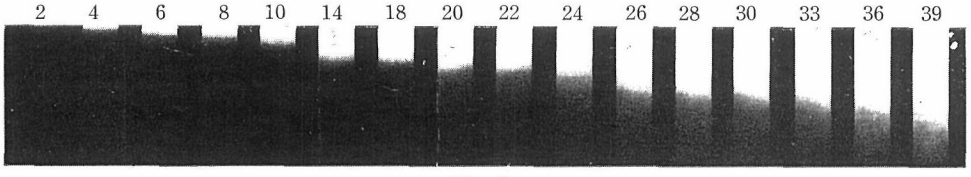

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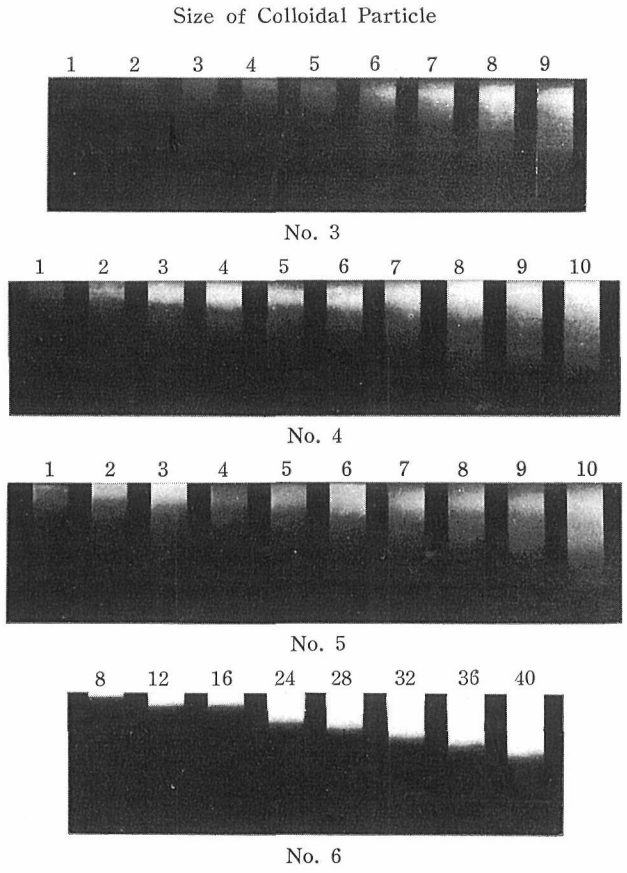


Fig. 1. Series of sedimentation photographs. The number on each window shows the time in minute, when the photograph was taken.

upon the method developed by Svedberg,[2] and will be explained hereunder with respect to the sample No. 2. The revolution speed of the rotor was 12,959 r.p.m. and the exposures were made at intervals of 2 minutes. The microphotometric curve of the sedimentation photograph was taken, and the intensity *versus*

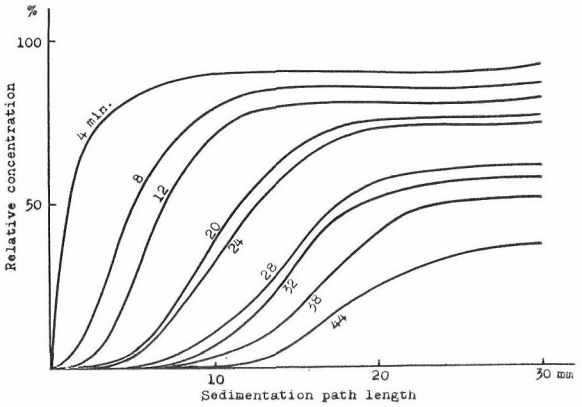


Fig. 2 A. series of relative concentration-path length curve of sedimenting gold sol No. 2.

sedimenting path-length curve was converted into the concentration *versus* sedimenting path-length curve (Fig. 2) by the Beer-Lambert formula $\left(\ln\frac{I_0}{I_x}=kC_x\right)$, where the abscissa shows the distance from the meniscus to the bottom of the cell and the oridinate shows the locally varying concentration of the sol in the cell and the length is enlarged as twice larger than the actual

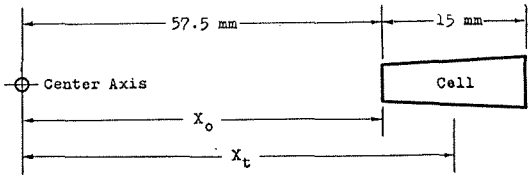


Fig. 3. Actual size and relating quantities of the rotor in the ultracentrifuge.

length. The actual size of the essential part of the rotor is shown in Fig. 3. The distance of the top of the cell from the center axis of revolution is 57.5mm, and the cell length is 15mm. If the distances from the meniscus to the center axis of revolution changed from x_0 which is the initial position of the meniscus x_t during a lapse of time from $t=0$ to $t=t$, the following equations can be given :

$$x_t = x_0 e^{S\omega^2 t}$$

$$\frac{\ln\frac{x_t}{x_0}}{\omega^2} = St \qquad (1)$$

$$\omega = 2\pi Z/60,$$

where S is usually called the sedimentation constant and Z is the number of revolution of the rotor per minute.

For the value of x_t, the position (x_t'), where the concentration corresponds to a half of the saturated one in the neighborhood of the bottom of the cell, was taken on each curve in Fig. 2. The value of x_t is equal to the sum of

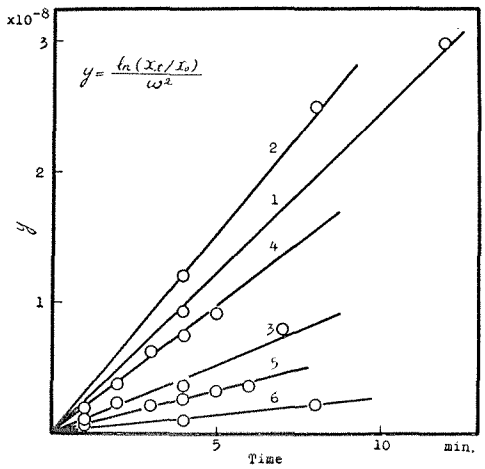


Fig. 4. The linear relationship giving the sedimentation constants.

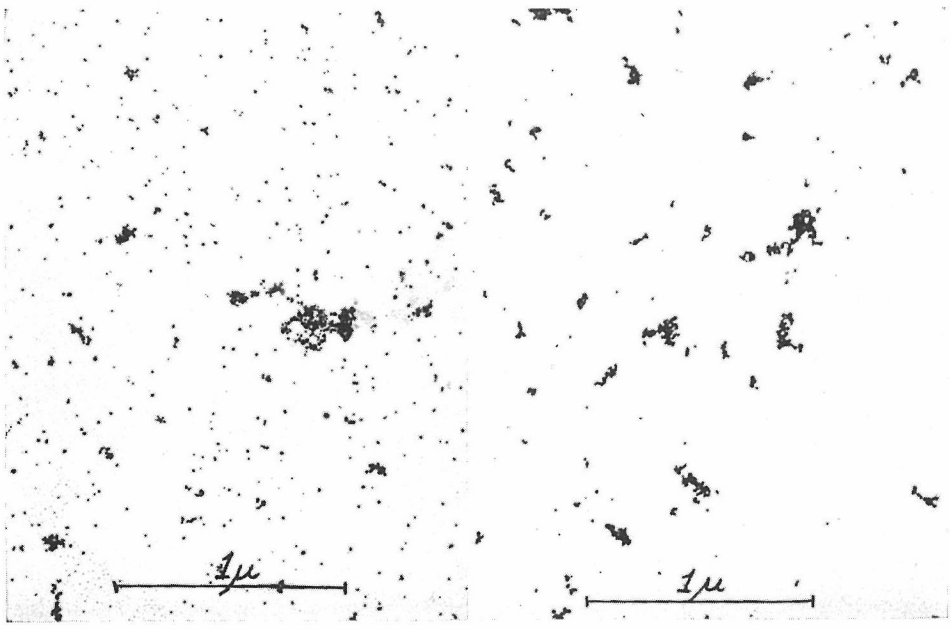
two values, x_t' and the distance between the center axis of revolution and the top of the cell (=57.5mm). The value of $\frac{\ln (x_t/x_0)}{\omega^2}$ was calculated by Eq. 1. By the plot of this value on the ordinate against the value of time t on the abscissa, curves were obtained as shown in Fig. 4. From these curves, the inclination, which is also the sedimentation constant itself, can be obtained. The result is shown in Table 1. On the other hand, it is well known that the relationship between the diameter of the particle D_s and the sedimentation constant S is given by the following equation :

$$D_s = 2r = \sqrt{18 \frac{\eta S}{\rho' - \rho}} \quad , \tag{2}$$

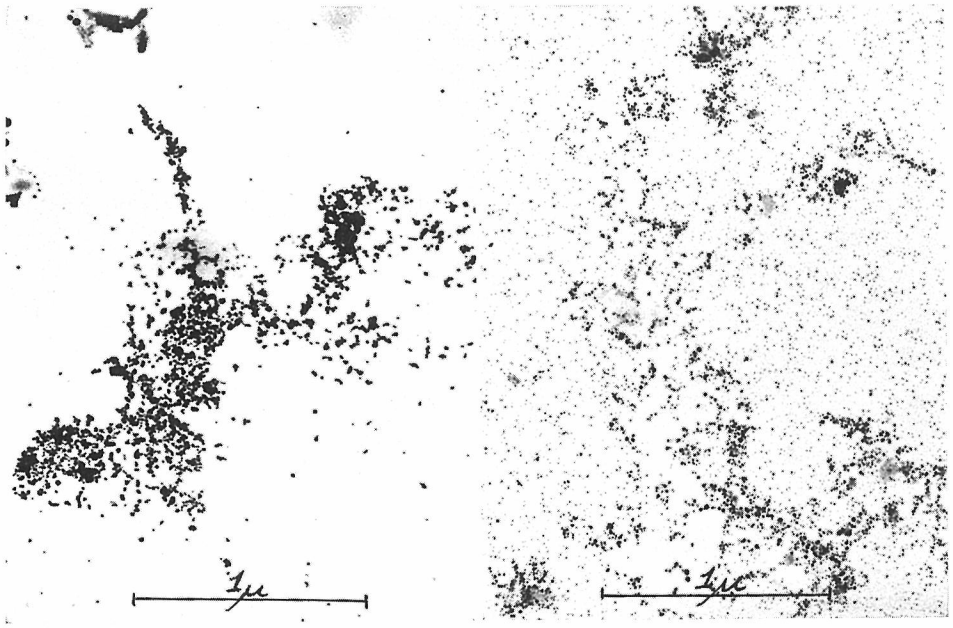
where ρ, ρ', and η are the density of the suspension medium, that of the dispersed particle, and the viscosity of the medium, respectively. By this equation, the diameter of the particle was calculated. The result is also shown in Table 1.

IV. ELECTRON MICROSCOPY

The electron microphotographs of the same specimens were taken as presented in Fig. 5. The electron microscope used here is TRS-50, and the resolving power of the apparatus is estimated to be about 20 Å. The magnification was corrected with Dow polystylene latex,[3] whose diameter was precisely evaluated. The particle size distribution curves[4] are constructed by measuring the diameter of each particle taken in these photographs, as shown in Fig. 6. The modal diameter (D_m) corresponding to the maximum of the particle size distribution curve,



No. 1 No. 2



No. 3 No. 4

Fig. 5. Electron micrographs of the dispersed particles of gold sol Nos. 1, 2, 3 and 5.

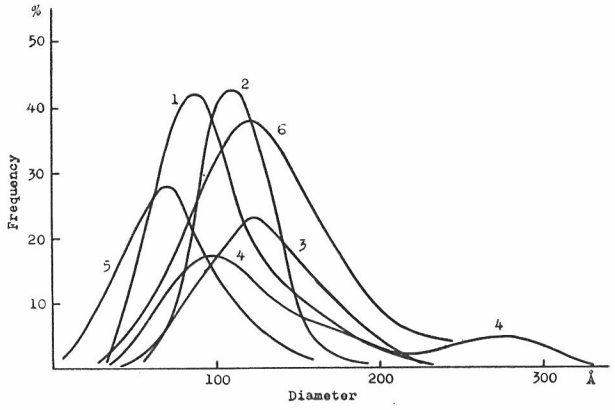


Fig. 6. Particle size distribution curves obtained by the electron micrographs.

and the average surface diameter (D_m) which was statistically calculated with respect to the same distribution curve, is shown in Table 1.

V. CONSIDERATION

The mean diameter of the particles obtained by the ultracentrifugal method has a tendency to take smaller value when compared with the one obtained from the electron micrograph. As shown in Fig. 6, the size distribution curve

of gold sol No. 4, which was obtained from the electron micrograph has two maxima. In this case, the mean diameter changes from 177 Å to 130 Å and approaches to the D_s value, when the higher maximum of the diameter is neglected, as the particle whose size is distributed in such a region is considered to have been sedimented at the ealier stage of the ultracentrifugal measurement.

The fact that the mean value obtained by the ultracentrifugal method becomes smaller than another mean values is considered to be effected by the following factors :

(1) In the case of the ultracentrifugation, a monodispersed sol gives a sharp boundary of the meniscus in the sedimentation cell. On the contrary, however, as in the present case, a polydispersed system gives a diffused one which in turn becomes the origin of the experimental error.

(2) In the case of the ultracentrifugation, the velocity of the sedimentation at an arbitrary position x is given by the following equation for a particle whose radius is given by r :

$$\frac{dx}{dt} = \frac{2}{9}\frac{r^2(\rho'-\rho)}{\eta}\omega^2 x = k\omega^2, \tag{3}$$

where k represents the constant value, $\frac{2}{9}\frac{r^2(\rho'-\rho)}{\eta}$. Then, the time τ needed for the particle to be completely sedimented away to the bottom of the cell is given by

$$\tau = \frac{1}{k\omega^2}\ln\frac{x_B}{x_0}, \tag{4}$$

where x_B is the distance from the centre axis of revolution to the bottom of the cell. Table 2 shows the relationship between the particle size and the time

Table 2.

D (Å)	τ (min.)
4	55
6	25
8	13.8
10	8.8
12	6.2
14	4.5
16	3.5
18	2.7
20	2.2
22	1.8
24	1.7

needed for the corresponding particle to be completely sedimented to the bottom of the cell, with respect to the sample No. 3 for an example. It becomes clear that all of the particles which are larger than 20 Å in diameter are completely sedimented within 2 minutes. Then, D_s value shifts to the larger one than

the actual mean diameter, as the larger particles are often missed out to be measured by the centrifugal method, and it is considered that the degree of the shifting will become more extensive as the particle size distributes over a wide range. On such a standpoint, the standard deviation (σ) and the value of

Table 3.

No.	2	1	5	3	6	4
σ	2.2	2.7	3.0	3.6	4.6	6.5
D_3/D_s	1.8	2.0	2.7	3.7	2.4	3.0

D_3/D_s were calculated with respect to all of the samples as shown in Table 3. Except for the last two samples, Nos. 6 and 4, the order of the standard deviation coincides with that of the value of D_3/D_s. In the case of the sample No. 6, iron hydroxide sol, even the comparatively larger particle is not sedimented so rapidly as in the case of the gold sol and it takes at least a few minutes, owing to the smaller density of the particle itself. This saved the larger particles from being missed out before the measurment is started at the outset of the revolution of the rotor and in turn makes the D_3/D_s value become smaller in spite of the comparatively large value of the standard deviation. As for the sample No. 4, it has two maxima in the size distribution curve, and is considered to show complicated behavior.

(3) In the case of the electron microscopy, the particle whose diameter is smaller than the resolution limit of the apparatus, that is, in ordinary case, a few ten angstroms often becomes the origin of the experimental error. As in the present work, most of the particles do not exceed 100 A, the effect of such a resolution limit is not a little, which causes the smaller particles to be missed out from being measured, quite on the contrary to the previous method. And, D_m as well as D_3 is often estimated to be larger than actual values.

VI. CONCLUSION

Accorrding to the previous consideration, the experimental errors are contained in both methods. But, fortunately the sign of these two kinds of errors is quite contrary to each other, then these two values, D_s and D_m (or D_3) become the lower and the upper limits of the actual mean particle size repectively. And the actual value is considered to be contained between these two kinds of mean diameters. Furthermore, the two kinds of particle size always do not so much deviate from each other as to be in quite different order of the value. This suggests that these colloidal particles are well dispersed in a sol and not in a state of cluster even when they are sedimented in the ultracentrifugal force field.

ACKNOWLEDGEMENT

The authers would like to express their sincere thanks to Mr. H. Inagaki

and Mr. F. Imagawa, Horio Laboratory of this Institute, for their preparation of the sedimentation photographs and their valuable discussions.

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